Aliphatic and Aromatic Sulfonates of Phenyloctadecane

By B. B. Schaeffer[2] and A. J. Stirton

The barium salts of sulfonic acids related to the phenylstearic acid of Nicolet and de Milt[3] were prepared for the purpose of coöperating with the Naval Research Laboratory,[4] in evaluating lubricating oil additives. The steps in the synthesis of barium phenyloctadecanesulfonate and of barium octadecylbenzenesulfonate are described below. In the Friedel and Crafts reaction of benzene with oleic acid, oleyl alcohol or an alkyl oleate, in the presence of aluminum chloride, the product is a viscous oil which does not easily crystallize. Apparently it is a mixture of at least two isomers (the 9- and the 10-phenyl derivatives).[5] The double bond may migrate during the reaction to increase the number of possible isomers. The sulfation of oleic acid, an analogous reaction, leads not only to 9- and 10-hydroxystearic acids but also to other isomeric hydroxy acids.[6]

Experimental

Phenyloctadecanol.—Phenyloctadecanol may be prepared from an alkyl phenylstearate or from oleyl acetate as described by Sisley,[7] but it is more readily prepared directly from oleyl alcohol. Oleyl alcohol, purity 83.4%, 0.58 mole, was dissolved in 500 ml. of benzene and added gradually over a period of four hours to a stirred suspension of 0.64 mole of aluminum chloride in 225 ml. of benzene at not over 35°. The mixture was heated and stirred for ten hours at 65°, cooled and hydrolyzed with dilute hydrochloric acid. Phenyloctadecanol was isolated as a fraction distilling at 180–198° at 0.15 mm., $n^{19}D$ 1.4940. The yield was 62%. The over-all yield was lower when phenyloctadecanol was prepared from oleyl acetate (31%) or by the Bouveault–Blanc reduction of butyl phenylstearate (17%).

Phenyloctadecyl Bromide.—Dry hydrogen bromide, generated by the action of bromine on tetralin, was led into 1.4 moles of phenyloctadecanol for a period of nine hours at 100–110° until 1.64 moles had been absorbed. The mixture was washed successively with sulfuric acid, 50% methanol, 15% aqueous ammonia and 50% methanol, separated and dried over calcium chloride and then fractionated by vacuum distillation. Phenyloctadecyl bromide was isolated as a yellow oil distilling at 182–194° at 0.02 mm., $n^{20}D$ 1.4995. The yield was 45%.

Anal.[8] Calcd. for $C_{24}H_{41}Br$: Br, 19.52. Found: 19.59.

The method using phosphorus tribromide in carbon tetrachloride led to greater emulsion difficulties, contamination with phosphorus compounds, under-bromination, and the necessity of separating the bromide from the alcohol when both were high boiling liquids.

Phenyloctadecyl Mercaptan.—The bromide was converted to the mercaptan by thiourea by the method of Urquhart, Gates and Connor[9] in a yield of 79%. Phenyloctadecyl mercaptan was isolated as an almost colorless oil with a slight mercaptan odor, distilling at 203–211° at 0.5 mm., $n^{25}D$ 1.4988, d^{25}_4 0.9066.

Anal. Calcd. for $C_{24}H_{42}S$: S, 8.84; mol. refr., 117.12. Found: S, 8.55; mol. refr., 117.36.

Barium Phenyloctadecanesulfonate.—The mercaptan (0.1 mole) was oxidized in acetone solution by the gradual addition of 0.7 mole of potassium permanganate during three hours of refluxing. Acetone was removed, concentrated hydrochloric acid was added to the residue, and the mixture was extracted with ethyl ether. The ether layer was continuously extracted with water for seventy-two hours. The aqueous extract was neutralized with sodium hydroxide and evaporated; the residue was dissolved in water and precipitated with barium chloride. The precipitate was washed with alcohol, dissolved in xylene and reprecipitated with acetone as barium phenyloctadecanesulfonate, a yellow hygroscopic solid. The yield was 27%.

Anal. Calcd. for $C_{48}H_{82}O_6S_2Ba$: Ba, 14.36. Found: Ba, 14.11.

Phenyloctadecane.—Phenyloctadecyl bromide (0.27 mole) was added dropwise during thirty minutes to 0.3 mole of magnesium turnings in 500 ml. of anhydrous ethyl ether. The mixture was warmed slightly to start the reaction, then refluxed for four hours. The flask was surrounded by an ice-bath, and the contents were hydrolyzed by the careful addition of 100 ml. of a cold 14% ammonium chloride solution, followed by 100 ml. of 5% hydrochloric acid. The ether solution was washed until the washings were neutral, and dried over sodium sulfate; then the ether was removed and the residue vacuum distilled. Phenyloctadecane was obtained as an almost colorless liquid, distilling at 145–152° at 0.08 mm., $n^{20}D$ 1.4862, d^{20}_4 0.8744. Molecular refractivity: theoretical, 109.43; found, 108.61. The yield was 49%.

Barium Octadecylbenzenesulfonate.—Phenyloctadecane (0.2 mole) was added dropwise during fifteen minutes with stirring to 157 g. of concentrated sulfuric acid, the temperature rising to 36°. The mixture was heated and stirred for two hours at 50°, cooled, poured into water and then extracted with ethyl ether. The ether layer was extracted with water, the water extract was neutralized with sodium hydroxide, evaporated and extracted with alcohol, and the alcoholic solution was evaporated, yielding the crude sodium salt. The crude sodium salt was converted to the barium salt by barium chloride, and barium octadecylbenzenesulfonate was isolated as a yellow hygroscopic solid. The yield was 41%.

Anal. Calcd. for $C_{48}H_{82}O_6S_2Ba$: Ba, 14.36. Found: Ba, 14.38.

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(4) Anacosta Station, Washington, D. C.

(5) Harmon and Marvel, This Journal, **54**, 2515 (1932).

(6) Schaeffer, Roe, Dixon and Ault, *ibid.*, **66**, 1924 (1944).

(7) Sisley, *Chim. industrie*, Special No., 763 (April, 1934)

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